

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-035916

(43)Date of publication of application : 09.02.1999

(51)Int. Cl.

C09J163/00

H05K 3/38

H05K 3/46

(21)Application number : 09-194221

(71)Applicant : SUMITOMO BAKELITE CO LTD

(22)Date of filing : 18.07.1997

(72)Inventor : KAMISAKA MASAO
HOZUMI TAKESHI

(54) LAYER INSULATION ADHESIVE FOR MULTILAYER PRINTED WIRING BOARD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an insulating adhesive which is excellent in the storage stability in a coated condition and shows good integral curability in the lamination on a substrate for an internal layer circuit, by incorporating a polyethersulfone having a specific molecular weight, an epoxy resin having a specific epoxy equivalent and a curing agent for an epoxy resin, as essential components.

SOLUTION: Polyethersulfone A has a weight average molecular weight of 103 to 105. The modification of a terminal present in this compound with a hydroxyl group, a carboxyl group or an amino group results in raising the reactivity thereof with an epoxy resin. Epoxy resin B has an epoxy equivalent of 500 or less. For example, an epoxy resin derived from bisphenol A is used. For imparting flame retardancy, a brominated epoxy resin is used. As an epoxy resin, an imidazole compound (for example, 2-methylimidazole) is preferred. Components A and B are compounded in an amount of 10 to 90 wt.%, respectively, based on the total amount of this insulating adhesive.

LEGAL STATUS

[Date of request for examination] 28.06.2000

[Date of sending the examiner's decision of rejection] 21.01.2003

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection] 2003-02655

[Date of requesting appeal against examiner's decision of rejection] 20.02.2003

[Date of extinction of right]

Copyright (C), 1998,2003 Japan Patent Office

ins. layer

≤ 40% silica⁴

10-90% PES³

Ex 1 PES MW 24,000

im
any hard

AN 1999:104719 CAPLUS
 DN 130:183457
 ED Entered STN: 16 Feb 1999
 TI Epoxy resin-based dielectric adhesives for multilayer printed circuit boards
 IN Kamisaka, Masao; Hozumi, Takeshi
 PA Sumitomo Bakelite Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 6 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C09J163-00
 ICS H05K003-38; H05K003-46
 CC 38-3 (Plastics Fabrication and Uses)
 Section cross-reference(s): 76

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 11035916	A2	19990209	JP 1997-194221	19970718 <--
	JP 3669663	B2	20050713		
	JP 2005248179	A2	20050915	JP 2005-55244	20050301
	JP 3703143	B2	20051005		
PRAI	JP 1997-194221	A3	19970718		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 11035916	ICM	C09J163-00
	ICS	H05K003-38; H05K003-46
	IPCI	C09J0163-00 [ICM,6]; H05K0003-38 [ICS,6]; H05K0003-46 [ICS,6]
JP 2005248179	IPCI	C09J0181-06 [ICM,7]; C09J0007-02 [ICS,7]; C09J0163-00 [ICS,7]; C09J0163-02 [ICS,7]; C09J0163-04 [ICS,7]; H05K0003-46 [ICS,7]
	FTERM	4J004/AA11; 4J004/AA13; 4J004/AB05; 4J004/CA08; 4J004/FA05; 4J004/FA08; 4J040/EC001; 4J040/EC061; 4J040/EC071; 4J040/EC161; 4J040/EJ031; 4J040/GA14; 4J040/HB22; 4J040/HC23; 4J040/KA09; 4J040/KA16; 4J040/LA08; 4J040/MA02; 4J040/NA20; 5E346/AA06; 5E346/AA16; 5E346/CC09; 5E346/CC32; 5E346/DD03; 5E346/DD12; 5E346/DD32; 5E346/EE33; 5E346/GG28; 5E346/HH18

AB The title adhesives, with good heat and fire resistance, elec. properties, and storage stability, contain polyether-polysulfones with weight-average mol. weight 103-105, epoxy resins with epoxy equivalent <500, and epoxy resin hardeners (e.g., 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, methyltetrahydrophthalic anhydride, Me end methylene tetrahydrophthalic anhydride).

ST epoxy resin polyether polysulfone dielec adhesive; multilayer printed circuit board dielec adhesive; imidazole deriv hardener epoxy resin dielec adhesive; anhydride hardener epoxy resin dielec adhesive

IT Electric insulators
 Electric insulators

(adhesives; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Adhesives
 Adhesives

(dielec.; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Anhydrides

RL: RCT (Reactant); TEM (Technical or engineered material use); RACT (Reactant or reagent); USES (Uses)

(epoxy resin hardeners; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Crosslinking agents

im
only
hard

(epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Adhesives
(heat-resistant; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Printed circuit boards
(multilayer; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Epoxy resins, uses
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(phenolic, novolak, brominated; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Polysulfones, uses
Polysulfones, uses
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(polyether-; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT Polyethers, uses
Polyethers, uses
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(polysulfone-; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT 85-42-7, Hexahydrophthalic anhydride 670-96-2, 2-Phenylimidazole
693-98-1, 2-Methylimidazole 827-43-0, 2-Phenyl-4-methylimidazole
931-36-2, 2-Ethyl-4-methylimidazole 13682-32-1 25134-21-8
25550-51-0, Methylhexahydrophthalic anhydride 26590-20-5,
Methyltetrahydrophthalic anhydride 61698-32-6 116820-11-2
RL: RCT (Reactant); TEM (Technical or engineered material use); RACT
(Reactant or reagent); USES (Uses)
(epoxy resin hardeners; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT 65581-98-8, Epiclon 830 93195-67-6, BREN-S 114731-82-7, ELM-100
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

IT 7440-50-8, Copper, uses
RL: NUU (Other use, unclassified); USES (Uses)
(foils; epoxy resin-based dielec. adhesives for multilayer printed circuit boards)

DERWENT-ACC-NO: 1999-186564

DERWENT-WEEK: 200573

COPYRIGHT 2006 DERWENT INFORMATION LTD

TITLE: Adhesive agent for multilayered printed circuits has insulated layers which consist of predefined quantity of polyether sulfone, epoxy resin and epoxy resin hardener

PATENT-ASSIGNEE: SUMITOMO BAKELITE CO LTD[SUMB]

PRIORITY-DATA: 1997JP-0194221 (July 18, 1997)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAINIPC
<u>JP 11035916 A</u>	February 9, 1999	N/A	006	C09J 163/00
JP 3669663 B2	July 13, 2005	N/A	008	C09J 163/00

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 11035916A	N/A	1997JP0194221	July 18, 1997
JP 3669663B2	N/A	1997JP0194221	July 18, 1997
JP 3669663B2	Previous Publ.	JP 11035916	N/A

INT-CL (IPC): C09J163/00, H05K003/38 , H05K003/46

RELATED-ACC-NO: 2005-707466

ABSTRACTED-PUB-NO: JP 11035916A

BASIC-ABSTRACT:

NOVELTY - The adhesive agent (4) has insulated layers (1,2) which consist of polyether sulfone of weight average molecular weight of 1000100000, an epoxy resin of 500 epoxy equivalent and an epoxy resin hardener.

USE - For multilayered printed circuits (claimed).

ADVANTAGE - The adhesive agent has excellent heat, fire and moisture resistances and has durability.

CHOSEN-DRAWING: Dwg.1/1

TITLE-TERMS: ADHESIVE AGENT MULTILAYER PRINT CIRCUIT INSULATE LAYER CONSIST PREDEFINED QUANTITY POLYETHER SULPHONE POLYEPOXIDE RESIN EPOXY RESIN HARDEN

DERWENT-CLASS: A85 G03 L03 V04

CPI-CODES: A05-A01E2; A05-J06; A12-E07C; G03-B02E; G03-B02E2; L03-H04E;

EPI-CODES: V04-R05A; V04-R07P1;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; P1047 P0964 P1490 H0260 F34 F61 D01 ; M9999 M2391 ; M9999 M2153*R ; M9999 M2062 ; M9999 M2324

Polymer Index [1.2]

018 ; ND01 ; Q9999 Q6644*R ; Q9999 Q7454 Q7330 ; K9745*R ; K9676*R ; K9552 K9483 ; B9999 B4717 B4706 B4568 ; B9999 B4682 B4568 ; B9999 B4239 ; B9999 B5287 B5276 ; N9999 N7147 N7034 N7023

Polymer Index [1.3]

018 ; B9999 B5094 B4977 B4740

Partial Translation of
Japanese Patent Application No. 11-35916

[0005]

[Means for Achieving the Object] The present invention relates to an interlayer insulation adhesive for multilayered printed wiring board characterized by containing the following components as essential components:

- (i) polyether sulfone having a weight average molecular weight of 10^3 to 10^5 ,
- (ii) epoxy resin having an epoxy equivalent of 500 or below, and
- (iii) an epoxy resin curing agent.

Polyether sulfone having a weight average molecular weight of 10^3 - 10^5 of (i) component, is mixed for the purposes of reducing softening of the insulation adhesive at the time of formation, maintaining the thickness in the laminated insulation layer, assigning flexibility to the insulation layer, and making the insulation layer highly heat-resistant. Moreover, the insulation adhesive is also considered to improve flame resistance and electric characteristics. The rate of the high-molecular-weight polyether sulfone is 10 to 90% by weight based on the entire insulation adhesive. If the rate is smaller than 10 % by weight, the insulation layer is too softened by heat at the time of lamination and the interlayer thickness cannot be maintained. In addition, a problem arises that melt viscosity is too lowered at the time of heat curing and creases are thereby generated, etc. On the other hand, if the rate is higher than 90 % by weight, the adhesive composition becomes stiff and lacks elasticity. Thus, adhesion to an irregular surface of the base material is poor at the time of lamination and forming void is caused. In addition, if the terminal of the high-molecular-weight polyether sulfone is denatured with a hydroxyl group, a carboxyl group or an amino group, its reactivity with epoxy resin is preferable.

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the layer insulation agent for multilayer printed wiring boards, especially this invention is excellent in high thermal resistance, a high electrical property, fire retardancy, and preservation stability, and relates to the epoxy resin system layer insulation adhesives 100 degrees C or more which can be promptly hardened at an elevated temperature.

[0002]

[Description of the Prior Art] When manufacturing a multilayer printed wiring board conventionally, one or more prepreg sheets which it sank [sheets] into the glass-fabrics base material, and made it carry out semi-hardening of the epoxy resin on the inner layer circuit board in which the circuit was formed were piled up, copper foil was further piled up on it, and it has passed through the process of really [application-of-pressure] fabricating with a hot-platen press. However, in order to make the impregnating resin in prepreg re-flow with heat, to make it harden under a constant pressure, and to make homogeneity carry out hardening shaping, 1 - 1.5 hours is required of this process. Thus, in this top, the production process serves as high cost by the cost of a multilayer laminating press and glass-fabrics prepreg etc. for a long time. In addition, because of the approach of carrying out impregnation of the resin to glass fabrics, the thickness between circuitry layers was restricted by glass fabrics, and pole thinning of the whole multilayer printed wiring board was also difficult. In order to solve these problems in recent years, heating pressing by the hot-platen press is not performed, but the technique of the multilayer printed wiring board by the build up method in which glass fabrics are not used for layer insulation material attracts attention anew.

[0003]

[Problem(s) to be Solved by the Invention] this invention person is examining various methods of manufacturing a multilayer printed wiring board by low cost with the simplified build up method to the approach of fabricating with the above-mentioned hot-platen press. In the multilayer printed wiring board by the build up method, when a film-like layer insulation resin layer is used, in order to lose the insulating substrate, circuit, and level

difference of a inner layer circuit plate and to graduate the front face, it has become common to apply an under coat agent to a inner layer circuit plate. As this typical example, the under coat agent applied to the inner layer circuit plate laminates the copper foil which carried out the coat of the layer insulation adhesives in un-hardening, semi-hardening, or the condition of having hardened, and a multilayer printed wiring board is obtained by really hardening. By such approach, the lamination of the copper foil which carried out the coat of the layer insulation adhesives since the level difference by the circuit of a inner layer circuit plate became small is easy, and need's [of taking into consideration the copper foil survival rate of a inner layer circuit plate] decreases.

[0004] In such a process, the layer insulation adhesives by which the coat was carried out to copper foil become soft too much at the time of lamination shaping, and layer-to-layer thickness cannot be secured. At the time of heat curing, melt viscosity falls too much and a wrinkle occurs. Moreover, the hardening reaction advanced at the time of the preservation, and when laminated to the inner layer circuit plate with which the under coat agent was applied, the problem referred to as that shaping is not really performed good has arisen. Furthermore, although the trouble of being difficult also has flameproofing since the glass fiber base material is not used for layer insulation adhesives, about these points, Japanese Patent Application No. No. 228433 [seven to] by these people etc. is already solved. However, it is not fully satisfied with former invention of the thermal resistance required of the build up material accompanying the densification of a multilayer printed wiring board. This invention is examined in order to solve this problem, and it is completed.

[0005]

[Means for Solving the Problem] This invention relates to the layer insulation adhesives for multilayer printed wiring boards characterized by containing each following component as an indispensable component.

(b) In a 500 or less weight per epoxy equivalent epoxy resin, an epoxy resin (Ha) curing agent, and this invention the polyether ape phone of weight average molecular weight 103-105, and (**)-- Although blended for the object of making small softening of the insulating adhesives at the time of shaping the polyether ape phone of the weight average molecular weight 103-105 of a (b) component, and maintaining the thickness of the insulating layer after a lamination, giving flexibility to an insulating layer, and a raise in the heatproof of an insulating layer Furthermore, it is expected that fire retardancy and an electrical property are also raised. A this amount polyether ape phone [of macromolecules] rate is 10 - 90 % of the weight to the whole insulating adhesives. If fewer than 10 % of the weight, it softens too much with heating at the time of lamination shaping, and thickness between layers cannot be secured. Moreover, melt viscosity falls too much at the time of heat curing, and the problem of a wrinkle occurring arises. On the other hand, since an adhesives constituent lacks in resiliency firmly when [than 90 % of the weight] more, the flattery nature to the irregularity at the time of lamination shaping and adhesion are bad, and cause shaping void generating. Moreover, while stopping the phase separation of a polyether ape phone and an epoxy resin after heat curing since reactivity with an epoxy resin is also good if the this amount polyether ape phone [of giant molecules] end has denaturalized by the hydroxyl group, the carboxyl group, or the amino group, the thermal

resistance of a hardened material is also raised. For this reason, it is desirable to perform the above-mentioned denaturation.

[0006] In order to carry out a coat to that it is smeared at the time of a roll lamination, and a sex and adhesion are missing, that the adhesive property after a lamination is not enough, causing destruction of a base material by the hot melt method, and copper foil, when it dissolves in a solvent and considers as the varnish of predetermined temperature, viscosity is high, it is smeared at the time of a coat, and neither a sex nor workability is [amount polyether ape phone of macromolecules independent / above-mentioned] good. In order to improve such a fault, 500 or less weight per epoxy equivalent epoxy resin (b) is blended. This blending ratio of coal is 10 - 90% of the weight of the whole resin. It becomes impossible to expect the above-mentioned effectiveness at 10 or less % of the weight, and to expect said amount polyether ape phone [of macromolecules] effectiveness at 90 % of the weight or more.

[0007] (b) As an epoxy resin of a component, although there are the bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, an aminophenol mold epoxy resin, etc., for fire-resistant grant besides the above-mentioned object, the bromination epoxy resin which is 20% or more of rates of bromination is desirable. The multilayer printed wiring board obtained as it is less than 20% of rates of bromination cannot attain fire-resistant V-0. If what was brominated is used, flameproofing of a multilayer printed wiring board will be performed more effectively.

[0008] Next, although especially the epoxy resin curing agent of a component (Ha) is not limited [acid anhydride / an amine compound, an imidazole compound,], since loadings can fully stiffen an epoxy resin at least and can demonstrate the fire retardancy of a bromination epoxy resin, an imidazole compound is desirable. The solubility to an epoxy resin is small, it is a solid in ordinary temperature with a melting point of 130 degrees C or more, and an epoxy resin and especially its thing that reacts promptly are [an imidazole compound becomes an elevated temperature 150 degrees C or more, and] desirable. Specifically, there is 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, a screw (2-ethyl-4-methylimidazole), 2-phenyl-4-methyl-5-hydroxymethylimidazole, 2-phenyl-4, 5-dihydroxymethylimidazole, or a triazine addition mold imidazole. These imidazoles are distributed by homogeneity in an epoxy resin varnish as impalpable powder. Since compatibility with an epoxy resin is small, at ordinary temperature -100 degree C, a reaction does not advance, therefore preservation stability can be kept good. And if it heats at 150 degrees C or more at the time of lamination hardening, it will react with an epoxy resin and a uniform hardened material will be obtained.

[0009] As a curing agent, in addition, phthalic anhydride, an anhydrous tetrahydrophthalic acid, an anhydrous methyl tetrahydrophthalic acid, Methyl endo-methylene-tetrahydrophthalic anhydride, an anhydrous methyl butenyl tetrahydrophthalic acid, Anhydrous hexahydrophthalic acid, anhydrous methyl hexahydrophthalic acid, anhydrous hexahydrophthalic acid, Acid anhydrides, such as trimellitic anhydride, pyromellitic dianhydride, and anhydrous benzophenone tetracarboxylic acid, the amine complex of a boron trifluoride, a dicyandiamide, or its derivative is mentioned, and what adduct[epoxy

]ized these, and the thing which microencapsulated can also be used. The component which reacts can be blended with the epoxy resin and curing agent other than the above-mentioned epoxy resin and a curing agent. For example, they are epoxy reactivity diluents (glycerol triglycidyl ether as 3 organic-functions molds, such as resorcinol diglycidyl ether and ethylene glycol glycidyl ether, as 2 organic-functions molds, such as phenyl glycidyl ether, as 1 organic-functions mold etc.), a resol mold or novolak mold phenol system resin, an isocyanate compound, etc.

[0010] Fused silica, a crystalline silica, a calcium carbonate, an aluminum hydroxide, an alumina, clay, a barium sulfate, a mica, talc, white carbon, E glass impalpable powder, etc. may be blended with everything but the above-mentioned component 40 or less % of the weight to a pitch for [, such as coefficient of linear expansion, thermal resistance, and burning resistance,] improvement. If it blends more mostly than 40 % of the weight, the viscosity of adhesives will become high and the embedded nature of a between [inner layer circuits] will come to fall. furthermore, the defoaming agent for preventing silane coupling agents, such as an epoxy silane, or a titanate system coupling agent, and a void, in order to heighten the adhesion force with copper foil or the inner layer circuit board or to raise moisture resistance -- or addition of a liquefied or impalpable powder type flame retarder is also possible.

[0011] After applying adhesives to copper foil and drying as a solvent, what does not remain into adhesives must be chosen. For example, an acetone, a methyl ethyl ketone (MEK), toluene, a xylene, n-hexane, a methanol, ethanol, methyl Cellosolve, ethyl Cellosolve, a cyclohexanone, dimethyl formamide (DMF), etc. are used. After it carries out coating of the adhesives varnish which dissolved the adhesives component in the predetermined solvent by predetermined concentration to the support side of copper foil, the copper foil with layer insulation adhesives performs 80 degrees C - 130 degrees C desiccation, and as a solvent does not remain, it produces it in adhesives. The thickness of the adhesives layer has desirable 15-120 micrometers. Although layer insulation nature is satisfactory if thicker [when thinner than 15 micrometers, layer insulation nature may become inadequate and] than 120 micrometers, it stops suiting the object of this invention that production is not easy and makes thickness of a multilayer board thin.

[0012] This copper foil with layer insulation adhesives is usually laminated in the inner layer circuit board with a dry film laminator, can be stiffened, and can form the multilayer printed wiring board which has an outer layer circuit easily. Next, the under coat agent used in order to lose the level difference by the circuit of the inner layer circuit board is described. In order to usually layer insulation adhesives and really stiffen an under coat agent, this and an ingredient of the same kind are used. Therefore, in this invention, an epoxy resin and the thing which uses a bromination epoxy resin as a principal component preferably are used. However, the varnish which dissolved in the solvent is sufficient and the varnish which dissolved in the reactant diluent which reacts by heat or light is sufficient. this under coat agent varnish -- a inner layer circuit plate -- applying -- subsequently -- heating -- evaporation or the reaction of a solvent -- the formation of tuck free thru/or prepolymer-izing, or the formation of tuck free carry out an optical exposure and according to a reaction -- or it prepolymer-izes.

[0013]

[Example]

The <example 1> end hydroxyl-group denaturation polyether ape phone (average molecular weight 24000) 100 weight section (all loadings express the weight section hereafter), the bromination phenol novolak mold epoxy resin 200 section (weight per epoxy equivalent 285, BREN-S by Nippon Kayaku Co., Ltd.), and the bisphenol female mold epoxy resin (weight-per-epoxy-equivalent 175, Epiclon 830 made from Dainippon Ink Chemistry) 100 section were stirred to the mixed solvent of MEK and DMF, and it dissolved. The 2-methylimidazole 5 section, the titanate system coupling agent (KR[by Ajinomoto Co., Inc.]-46B) 0.2 section, and the barium-sulfate 20 section were added as a curing agent there, and the adhesives varnish was produced.

[0014] Hereafter, the multilayer printed wiring board was produced at the process shown in drawing 1. It applied and dried with the roller coater and copper foil with insulating adhesives (3) was obtained so that the thickness after drying said adhesives varnish to the support side of copper foil (1) with a thickness of 18 micrometers might be set to 50 micrometers (a). Next, the bisphenol A mold epoxy resin (weight-per-epoxy-equivalent 470, weight average molecular weight 900 [about]) 100 section was dissolved in the glycidyl methacrylate 40 section, the 2-methylimidazole 3 section and the photopolymerization initiator (Ciba-Geigy IRUGA cure 651) 1.2 section were added as a curing agent to this, and it stirred enough, and considered as the under coat agent.

[0015] Furthermore, pattern processing of the glass epoxy double-sided copper clad laminate of 0.1mm of base material thickness and 35 micrometers of copper foil thickness was carried out, and the inner layer circuit plate was obtained. a copper foil front face -- melanism -- after processing, coating of the above-mentioned under coat agent was carried out to about 40 micrometers in thickness by the curtain coating machine. Then, they are about 2 J/cm² with two 80 W/cm high-pressure mercury-vapor lamps at UV conveyor. UV irradiation was carried out on conditions and the under coat agent was made tuck free. They are the temperature of 100 degrees C, pressure 4 kg/cm², and lamination speed about the above-mentioned copper foil with insulating adhesives on the inner layer circuit plate which has the layer of this under coat agent. According to 0.8m conditions for /, the above-mentioned copper foil with insulating adhesives was laminated using the hard roll, heat hardening was carried out for 30 minutes, and 150 degrees C of multilayer printed wiring boards were produced.

[0016] The multilayer printed wiring board was produced like the example 1 except having changed the imidazole used for <examples 2-3> layer insulation adhesives and an under coat agent from 2-methylimidazole, respectively to 2-phenyl-4-methylimidazole or 2-phenyl-4-methyl-5-hydroxymethylimidazole.

[0017] The multilayer printed wiring board was produced for the <example 4> end hydroxyl-group denaturation polyether ape phone (mean molecular weight 24000) 100 section, the bromination phenol novolak mold epoxy resin 70 section (weight per epoxy equivalent 285, BREN-S by Nippon Kayaku Co., Ltd.), and the bisphenol female mold epoxy resin (weight-per-epoxy-equivalent 175, Epiclon 830 made from Dainippon Ink Chemistry) 30 section like the example 1.

[0018] The <example 5> end hydroxyl-group denaturation polyether ape phone (mean molecular weight 24000) 100 section, the bromination phenol novolak mold epoxy resin 70 section (weight per epoxy equivalent 285, BREN-S by Nippon Kayaku Co., Ltd.), and the aminophenol mold epoxy resin (weight-per-epoxy-equivalent 107, Sumitomo Chemical Co., Ltd. make ELM-100) 35 section were stirred to MEK, and it dissolved. The methyl-cyclohexene-dicarboxylic-anhydride 35 section was added as a curing agent, the 2-phenyl-4-methyl-5-hydroxymethylimidazole 0.5 section, the titanate system coupling agent (KR[by Ajinomoto Co., Inc.]-46B) 0.2 section, and the barium-sulfate 20 section were added as a hardening accelerator there, the adhesives varnish was produced, and the multilayer printed wiring board was produced like the example 1.

[0019] The multilayer printed wiring board was obtained like the example 1 except having used the <example 1 of comparison> bromination phenoxy resin (25% [of rates of bromination], mean molecular weight 30000) 100 section, and the bisphenol female mold epoxy resin (weight-per-epoxy-equivalent 175, Epiclon 830 made from Dainippon Ink Chemistry) 50 section.

[0020] About the obtained multilayer printed wiring board, surface smooth nature, moisture absorption solder thermal resistance, the Peel reinforcement, and fire retardancy were measured, and the result shown in a table 1 was obtained.

(Table 1 characterization result)

	surface smooth nature	Moisture absorption	solder thermal resistance	Peel reinforcement	Glass transition temperature
example 1	5 micrometers	O 1.4 kg/cm	219 degrees C	Example 2	5 micrometers
		O 1.3 kg/cm	215 degrees C	Example 3	3 micrometers
		O 1.3 kg/cm	208 degrees C	Example 4	3 micrometers
		O 1.3 kg/cm	224 degrees C	Example 5	3 micrometers
		O 1.4 kg/cm	240 degrees C	Example 6 of a comparison	5 micrometers
		O 1.4 kg/cm	159degree-C		

----- [0021] (Measuring method)

inner layer circuit plate test piece: -- 150-micrometer pitch between lines, and clearance hole 1.0mm -- phi1. surface smooth nature:JIS B 0601 R (max)

2. Moisture absorption solder thermal-resistance moisture absorption conditions : the case where there were no all pressure cooker processing, 125 degrees C, 2.3 atmospheric pressures, and 30 minute test condition:n=5, and there was no bulging at 280 degrees C and 120-second Hazama was made into O.

3. Peel reinforcement : JIS C It is based on the loss tangent of 4. dynamic viscoelasticity measurement by 6486.

[0022]

[Effect of the Invention] Since hardening is really performed good when laminated in the inner layer circuit board to which the layer insulation adhesives for multilayer printed wiring boards of this invention were excellent in shelf life in the condition of having carried out the coat to the condition or copper foil of a varnish, and coating of the under coat agent was carried out, especially the obtained multilayer printed wiring board is excellent in thermal resistance, and has the property which was excellent in fire retardancy, moisture resistance, etc. not to mention the electrical property.

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Layer insulation adhesives for multilayer printed wiring boards characterized by containing each following component as an indispensable component.

(b) the polyether aepone of weight average molecular weight 103-105, and (**) -- a 500 or less weight per epoxy equivalent epoxy resin, an epoxy resin (Ha) curing agent, and

[Claim 2] (b) Layer insulation adhesives for multilayer printed wiring boards according to claim 1 whose component is weight average molecular weight 103-105 and whose end is the hydroxyl-group, carboxyl group, or polyether aepone of amino-group denaturation.

[Claim 3] (b) Layer insulation adhesives for multilayer printed wiring boards according to claim 1 or 2 whose component is 10 - 90% of the weight of the sum total weight of a (b) component and a (b) component.

[Claim 4] (b) Layer insulation adhesives for multilayer printed wiring boards according to claim 1, 2, or 3 components are one sort or two sorts or more of things chosen from the bisphenol mold epoxy resin, the novolak mold epoxy resin, and the aminophenol mold epoxy resin, and are [adhesives] 10 - 90% of the weight of the sum total weight of a (b) component and a (b) component.

[Claim 5] Layer insulation adhesives for multilayer printed wiring boards according to claim 1, 2, 3, or 4 whose epoxy resin curing agent is one sort chosen from 2-methyl imidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, a screw (2-ethyl-4-methyl) imidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole, the 2-phenyl -4, 5-hydroxymethyl imidazole, and the triazine addition mold imidazole, or two sorts or more.

[Claim 6] Layer insulation adhesives for multilayer printed wiring boards according to claim 1, 2, 3, or 4 whose epoxy resin curing agent is one sort of the acid anhydride chosen from methyl cyclohexene-dicarboxylic anhydride, methyl and methylene tetrahydro phthalic anhydride, methyl butenyl tetrahydro phthalic anhydride, hexahydro phthalic anhydride, and methyl hexahydro phthalic anhydride, or two sorts or more.

[Claim 7] Copper foil with layer insulation adhesives for multilayer printed wiring boards which comes to carry out the coat of the layer insulation adhesives according to claim 1, 2, 3, 4, or 5 to copper foil.

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-35916

(43) 公開日 平成11年(1999)2月9日

(51) Int. Cl. ⁶ C 0 9 J 1 6 3 / 0 0 H 0 5 K 3 / 3 8 3 / 4 6	識別記号	P 1 C 0 9 J 1 6 3 / 0 0 H 0 5 K 3 / 3 8 3 / 4 6	E G T
審査請求 未請求 請求項の数 7 O L (全 6 頁)			
(21) 出願番号	特願平9-194221		
(22) 出願日	平成9年(1997)7月18日		
(71) 出願人	000002141 住友ベークライト株式会社 東京都品川区東品川2丁目5番8号		
(72) 発明者	上坂 政夫 東京都品川区東品川2丁目5番8号 住友 ベークライト株式会社内		
(72) 発明者	八月朔日 猛 東京都品川区東品川2丁目5番8号 住友 ベークライト株式会社内		

(54) 【発明の名称】 多層プリント配線板用層間絶縁接着剤

(57) 【要約】

【課題】 耐熱性、保存安定性に優れ、かつ100℃以上の高温で速やかに硬化しうるエポキシ樹脂系層間絶縁接着剤を得ること。

【解決手段】 下記の各成分を必須成分として含有する多層プリント配線板用層間絶縁接着剤。

(1) 重畳平均分子量103~105のポリエーテルサルホン、(2) エポキシ当量500以下のエポキシ樹脂、(3) エポキシ樹脂硬化剤ポリエーテルサルホンは、水酸基、カルボキシル基あるいはアミノ基で変性されたものが好ましく、硬化剤はイミダゾール化合物が好ましい。

【特許請求の範囲】

【請求項1】 下記の各成分を必須成分として含有することを特徴とする多層プリント配線板用層間絶縁接着剤。

(イ) 重量平均分子量10³～10⁵のポリエーテルサルフォン、(ロ) エポキシ当量500以下のエポキシ樹脂、(ハ) エポキシ樹脂硬化剤、

【請求項2】 (イ) 成分が、重量平均分子量10³～10⁵であり、末端が水酸基、カルボキシル基又はアミノ基変性のポリエーテルサルフォンである請求項1記載の多層プリント配線板用層間絶縁接着剤。

【請求項3】 (イ) 成分が、(イ) 成分及び(ロ) 成分の合計重量の10～90重量%である請求項1又は2記載の多層プリント配線板用層間絶縁接着剤。

【請求項4】 (ロ) 成分が、ビスフェノール型エポキシ樹脂、ノボラック型エポキシ樹脂およびアミノフェノール型エポキシ樹脂から選ばれた1種または2種以上のもので、(イ) 成分及び(ロ) 成分の合計重量の10～90重量%である請求項1、2又は3記載の多層プリント配線板用層間絶縁接着剤。

【請求項5】 エポキシ樹脂硬化剤が、2-メチルイミダゾール、2-フェニルイミダゾール、2-フェニル-4-メチルイミダゾール、ビス(2-エチル-4-メチル)イミダゾール、2-フェニル-4-メチル-5-ヒドロキシメチルイミダゾール、2-フェニル-4、5-ヒドロキシメチルイミダゾールおよびトリアジン付加型イミダゾールから選ばれた1種または2種以上である請求項1、2、3又は4記載の多層プリント配線板用層間絶縁接着剤。

【請求項6】 エポキシ樹脂硬化剤が、メチルテトラヒドロ無水フタル酸、メチルエンドメチレンテトラヒドロ無水フタル酸、メチルブチレンテトラヒドロ無水フタル酸、ヘキサヒドロ無水フタル酸、メチルヘキサヒドロ無水フタル酸から選ばれた酸無水物の1種または2種以上である請求項1、2、3又は4記載の多層プリント配線板用層間絶縁接着剤。

【請求項7】 請求項1、2、3、4又は5記載の層間絶縁接着剤を銅箔にコートしてなる多層プリント配線板用層間絶縁接着剤付き銅箔。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は多層プリント配線板用層間絶縁剤に関し、特に高耐熱性、高電気特性、耐熱性、保存安定性にすぐれ、かつ、100℃以上の高温で速やかに硬化し得るエポキシ樹脂系層間絶縁接着剤に関する。

【0002】

【従来の技術】 従来、多層プリント配線板を製造する場合、回路が形成された内層回路基板上にガラスクロス基材にエポキシ樹脂を含浸して半硬化させたプリプレグシ

ートを1枚以上重ね、更にその上に銅箔を重ね熱板プレスにて加圧一体成形するという工程を経ている。しかし、この工程ではプリプレグ中の含浸樹脂を熱により再流動させ一定圧力下で硬化させるため、均一に硬化成形させるためには1～1.5時間は必要である。このように製造工程が長くなる上に、多層積層プレス及びガラスクロスプリプレグのコスト等により高コストとなっている。加えてガラスクロスに樹脂を含浸させる方法のため、回路層間の厚みがガラスクロスにより制限され多層プリント配線板全体の極薄化も困難であった。近年、これらの問題を解決するため、熱板プレスによる加熱加圧成形を行わず、層間絶縁材にガラスクロスを用いない、ビルドアップ方式による多層プリント配線板の技術が改めて注目されている。

【0003】

【発明が解決しようとする課題】 本発明者は、上記熱板プレスで成形する方法に対して、簡素化されたビルドアップ方式により多層プリント配線板を低コストで製造する方法を種々検討している。ビルドアップ方式による多層プリント配線板において、フィルム状の層間絶縁樹脂層を用いた場合、内層回路板の絶縁層と回路と段差を無くし、その表面を平滑化するために、内層回路板にアンダーコート剤を塗布することが一般化してきた。この代表的な例として、内層回路板に塗布されたアンダーコート剤が未硬化、半硬化または硬化した状態において、層間絶縁接着剤をコートした銅箔をラミネートし、一体硬化することにより多層プリント配線板を得る。このような方法により、内層回路板の回路による段差が小さくなるため、層間絶縁接着剤をコートした銅箔のラミネートが容易であり、また内層回路板の銅箔残存率を考慮する必要も少なくなる。

【0004】

このようなプロセスにおいて、銅箔にコートされた層間絶縁接着剤がラミネート成形時に軟化し過ぎて層間厚を確保できない、熱硬化時に溶融粘度が下がり過ぎて段が発生する。また、その保存時に硬化反応が進行して、アンダーコート剤が塗布された内層回路板にラミネートしたとき一体成形が良好に行われないうような問題が生じている。更に、層間絶縁接着剤にガラス繊維基材が使用されていないため、熱硬化が困難という問題点もあるが、これらの点については本出願人による特開平7-228433号、等により既に解決されている。しかし、以前の発明では多層プリント配線板の高密度化に伴う、ビルドアップ材に要求される耐熱性を十分に満足するものではない。本発明はかかる問題を改善するために検討し、完成されたものである。

【0005】

【課題を解決するための手段】 本発明は、下記の各成分を必須成分として含有することを特徴とする多層プリント配線板用層間絶縁接着剤に関するものである。

(イ) 重量平均分子量10³～10⁵のポリエーテルサル

フォン、(ロ)エポキシ当量500以下のエポキシ樹脂、(ハ)エポキシ樹脂硬化剤、本発明において、

(イ)成分の重量平均分子量10⁴~10⁵のポリエーテルサルフォンは、成形時の絶縁接着剤の硬化を小さくし、ラミネート後の絶縁層の厚みを維持すること、絶縁層に可塑性を付与すること、絶縁層の高耐熱化の目的で配合されているが、更に耐燃性、電気特性をも向上させると予想する。この高分子量ポリエーテルサルフォンの割合は絶縁接着剤全体に対して10~90重量%である。10重量%より少ないと、ラミネート成形時の加熱により軟化し過ぎて層間厚みを確保できない。また、熱硬化時に溶融粘度が下がり過ぎて破れが発生するなどの問題が生じる。一方、90重量%より多いと、接着剤組成物が固く弾力性に欠けるため、ラミネート成形時の凹凸への追従性、密着性が悪く、成形ボイド発生の原因となる。また、この高分子量ポリエーテルサルフォンの末端が水酸基、カルボキシ基あるいはアミノ基で変性されていれば、エポキシ樹脂との反応性も良いことから熱硬化後にポリエーテルサルフォンとエポキシ樹脂との相分離を抑えるとともに、硬化物の耐熱性も向上させる。このため上記変性が行われていることが望ましい。

【0006】上記高分子量ポリエーテルサルフォン単独では、ロールラミネート時の流れ性、密着性に欠けること、ラミネート後の接着性が十分でないこと、ホットメルト法では基材の破壊を招くこと、及び銅箔にコートするために溶剤に溶解して所定温度のワニスとしたときに、粘度が高く、コート時の流れ性や作業性が良くない。このような欠点を改善するためにエポキシ当量500以下のエポキシ樹脂(ロ)を配合する。この配合割合は樹脂全体の10~90重量%である。10重量%以下では上記の効果が期待できず、また、90重量%以上では前記高分子量ポリエーテルサルフォンの効果が期待できなくなる。

【0007】(ロ)成分のエポキシ樹脂としては、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂、アミノフェノール型エポキシ樹脂等があるが、上記の目的の他、難燃性付与のためには臭素化率20%以上である臭素化エポキシ樹脂が好ましい。臭素化率20%未満であると、得られた多層プリント配線板が難燃性V-0を達成することが出来ない。臭素化したものを使用すれば、多層プリント配線板の難燃化がより容易に行われる。

【0008】次に、(ハ)成分のエポキシ樹脂硬化剤は、アミン化合物、イミダゾール化合物、酸無水物など、特に限定されるものではないが、イミダゾール化合物は配合量が少なくてもエポキシ樹脂を十分に硬化させることができ、臭素化エポキシ樹脂の難燃性を発揮できるので好ましいものである。イミダゾール化合物は、融点130℃以上の高温で固形であり、エポキシ樹脂への

溶解性が小さく、150℃以上の高温になって、エポキシ樹脂と速やかに反応するものが特に好ましい。具体的には2-メチルイミダゾール、2-フェニルイミダゾール、2-フェニル-4-メチルイミダゾール、ビス(2-エチル-4-メチルイミダゾール)、2-フェニル-4-メチル-5-ヒドロキシメチルイミダゾール、2-フェニル-4、5-ジヒドロキシメチルイミダゾール、あるいはトリアジン付加型イミダゾール等がある。これらのイミダゾールは微粉末としてエポキシ樹脂ワニス中に均一分散される。エポキシ樹脂との相溶性が小さいので、常温~100℃では反応が進行せず、従って保存安定性を良好に保つことができる。そしてラミネート硬化時に150℃以上に加熱すると、エポキシ樹脂と反応し、均一な硬化物が得られる。

【0009】その他硬化剤として、無水フタル酸、無水テトラヒドロフタル酸、無水メチルテトラヒドロフタル酸、無水メチルエンドメチレンテトラヒドロフタル酸、無水メチルブチルテトラヒドロフタル酸、無水ヘキサヒドロフタル酸、無水メチルヘキサヒドロフタル酸、無水ヘキサヒドロフタル酸、無水トリメリット酸、無水ピロメリット酸、無水ベンゾフェノンテトラカルボン酸等の酸無水物、三フッ化ホウ素のアミン錯体、ジシアンジアミド又はその誘導体などが挙げられ、これらをエポキシアダクト化したものやマイクロカプセル化したものも使用できる。上記エポキシ樹脂及び硬化剤の他に、エポキシ樹脂や硬化剤と反応する成分を配合することができる。例えば、エポキシ反応性希釈剤(一言総称としてフェニルグリシジルエーテルなど、二官能型としてレゾルシンジグリシジルエーテル、エチレングリコールグリシジルエーテルなど、三官能型としてグリセロールトリグリシジルエーテルなど)、レゾール型又はノボラック型フェノール系樹脂、イソシアネート化合物などである。

【0010】上記成分の他に、線膨張率、耐燃性、耐熱性などの向上のために、溶融シリカ、結晶性シリカ、炭酸カルシウム、水酸化アルミニウム、アルミナ、クレー、硫酸バリウム、マイカ、タルク、ホウイットカーボン、Eガラス微粉末などを樹脂分に対して40重量%以下配合しても良い。40重量%より多く配合すると、接着剤の粘性が高くなり、内層回路間への浸透性が低下するようになる。さらに、銅箔や内層回路基板との密着力を高めたり、耐湿性を向上させるためにエポキシラン等のシランカップリング剤あるいはチタネート系カップリング剤、ボイドを防ぐための消泡剤、あるいは液状又は微粉末タイプの難燃剤の添加も可能である。

【0011】溶剤としては、接着剤を銅箔に塗布し乾燥した後に、接着剤中に残らないものを選択しなければならない。例えば、アセトン、メチルエチルケトン(MEK)、トルエン、キシレン、n-ヘキサン、メタノール、エタノール、メチルセルソルブ、エチルセルソルブ、シクロヘキサノン、ジメチルフォルムアミド(D

	表面平滑性	吸湿半田耐熱性	ピール強度	ガラス転移温度
実施例1	5 μ m	○	1.4 kq/cm	219℃
実施例2	5 μ m	○	1.3 kq/cm	215℃
実施例3	3 μ m	○	1.3 kq/cm	208℃
実施例4	3 μ m	○	1.3 kq/cm	224℃
実施例5	3 μ m	○	1.4 kq/cm	240℃
比較例6	5 μ m	○	1.4 kq/cm	159℃

【0021】(測定方法)

内層回路板試験片：線間150 μ mピッチ、クリアランスホール1.0mm ϕ

1. 表面平滑性：JIS B 0601 R(max)

2. 吸湿半田耐熱性

吸湿条件：プレッシャークッカー処理、125℃、2.3気圧、30分

試験条件：n=5で、全てが280℃、120秒間で膨れがなかった場合を○とした。

3. ピール強度：JIS C 6486による

4. 動的粘弾性測定：損失正接による。

【0022】

【発明の効果】本発明の多層プリント配線板用層間絶縁接着剤は、ワニスの状態あるいは銅箔にコートした状態において、保存性にすぐれ、アンダーコート剤が塗工さ

れた内層回路基板にラミネートしたとき一体化が良好に行われるので、得られた多層プリント配線板は特に耐熱性に優れ、電気特性はもちろんのこと、耐燃性、耐湿性等において優れた特性を有している。

【図面の簡単な説明】

【図1】 本発明の多層プリント配線板（一例）を作製する工程を示す概略断面図

【符号の説明】

- 1 内層回路板
- 2 内層回路
- 3 アンダーコート剤
- 4 熱硬化型絶縁接着剤
- 5 銅箔
- 6 硬質ロール
- 7 多層プリント配線板